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(54) Process for obtaining hulupones
from lupulones

(57) A process for obtaining hop extracts comprises adding adsorbents to hop products which contain alpha-acids and ground, crushed or ruptured lupulin seeds, or such hop products which are in the form of extracts, treating the mixture obtained with CO₂ in a closed pressure vessel at a supercritical temperature and under a pressure of from 50 to 600 bars, reducing the pressure of the CO₂ leaving the pressure vessel whereby a base extract comprising hop oils and lupulones is precipitated, mixing the lupulones with adsorbents, converting the lupulones to bitter-tasting hulupones by oxidation and treatment with CO₂ under pressure, and removing undesirably accompanying substances to purify the thus obtained hulupones. Hulupones obtained by the process, optionally in combination with isohumulones provide a beer-soluble product which, as a bitter constituent, has all the taste properties of natural hops.

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SPECIFICATION

Process for obtaining hulupones from lupulones

- 5 The present invention relates to a further development of the process described in British Patent Application No. 7921290, with the object of obtaining bitter-tasting hulupones from lupulones. In accordance with British Patent Application No. 7921290, an isomerised hop product may be obtained by adding adsorbents to hop products which contain alpha-acids and then treating the mixture in a pressure vessel at a supercritical temperature and under a pressure of from 50 to 80 bars. The isomerised product thus obtained is withdrawn from the pressure vessel in a dry form and the carbon dioxide, which causes the isomerisation also acts as a solvent and purifying agent. The carbon dioxide issuing from the pressure vessel contains, as dissolved substances, hop oils, soft hop resins, in particular beta-acids, and other indistinguishable soft resins. Under unfavourable operating conditions, it is also possible for small quantities of alpha-acids which have not been isomerised, to be removed from the pressure vessel in dissolved form with the carbon dioxide.

- According to the present invention it has now been found that, by reducing the pressure of the CO₂ which is led off from the pressure vessel, a pure, bitter-tasting hulupone product is obtained from the base extract which is precipitated in the pressure reduction vessel and of which about half consists of lupulones, by the addition of an adsorbent and an oxidising agent in conjunction with a further pressure treatment with CO₂, and also that this pure, bitter-tasting hulupone product can be added directly to beer or other beverages, including alcohol-free beverages, which are to be made bitter either on its own or together with other bitter constituents, such as isomerised alpha-acids which have been obtained by the process of British Patent Application No. 7921290.

- The lupulones or beta-acids are those hop resins which do not have a bitter taste, which are not isomerised in the brewing process and which are discarded thereafter, unused, together with the spent hops. From a quantitative point of view, the lupulone fraction of hops is as large as the humulone fraction thereof, and there has, therefore, been no lack of attempts to isolate the lupulones, either in the brewery itself or in conjunction with the preparation of isohumulones with the aid of organic solvents, and then to convert them into bitter-tasting hulupones.

- German Patent Specification No. 941,965 describes a process in which after the customary boiling of hops with wort, the spent hops which have been removed are oxidised with a controlled quantity of oxygen and are thereby converted into a bitter-tasting soft resin.

- German Auslegeschrift No. 1,300,485 is concerned with the conversion of lupulones into hulupones, and the hop resins, which have been dissolved in an organic solvent, are separated by means of a dilute aqueous alkaline solution into a lupulone-containing

phase and then oxidised by the passing in of oxygen. In accordance with the disclosure of German Offenlegungsschrift No. 2,217, 135, hulupones may be obtained from lupulones by oxidising the hop resins contained in a liquid alkaline medium with gases containing oxygen under the influence of visible light.

- In accordance with the disclosure of German Auslegeschrift No. 2,244,895, lupulones are oxidised catalytically to give hulupones by using finely divided noble metals or noble metal oxides as catalysts.

- In the procedure suggested here, an acceleration of the oxidation reaction was also observed in an alkaline, polar solution by increasing the pressure to 60 atmospheres gauge and also raising the temperature to approximately 100°C. However, because of the uncontrolled reaction, a yield of unpurified hulupone of only approximately 20% was obtained.

- All the processes mentioned above have the disadvantage that in addition to the desired end product, the resulting oxidation products contain undesirable by-products and therefore cannot be added directly to beer.

- It is the object of the present invention to obtain a bitter-tasting hulupone product in improved yield and without the disadvantages of undesirable by-products, so that it can be added directly to beer or to other beverages.

- According to the present invention there is provided a process for obtaining hop extracts which comprises adding adsorbents to hop products which contain alpha-acids and ground, crushed or ruptured lupulin seeds, or hop products which are in the form of extracts, treating the mixture obtained with CO₂ in a closed pressure vessel at a supercritical temperature and under a pressure of from 50 to 600 bars, reducing the pressure of the CO₂ leaving the pressure vessel whereby a base extract comprising hop oils and lupulones is precipitated, mixing the lupulones with adsorbents, converting the lupulones to bitter-tasting hulupones by oxidation and treatment with CO₂ under pressure, and removing undesirable accompanying substances to purify the thus obtained hulupones. Preferably, hop products in the form of extracts are used, these extracts most preferably being obtained by a process which comprises extracting hops or a hop product with CO₂ at a temperature up to its critical temperature and at a pressure above its critical pressure and subsequently evaporating the CO₂ from the extract obtained.

- In detail, the process according to the present invention may be carried out as follows:

- The base extract obtained on the pressure reduction side in the isomerisation of humulones in accordance with British Patent Application No. 7921290 essentially consists of hop oils, beta-acids and indefinable soft resins, esters and waxes. By removal in stages, the hop oils are separated in a nearly pure form from the other constituents of this base extract.

- This separation is appropriately effected in a second pressure reduction vessel which is placed downstream, and which reduces the pressure of the circulating CO₂ by means of a suitably adjusted

pressure reduction valve, to a lower pressure than that in the first pressure reduction vessel.

After isomerisation of the alpha-acid in accordance with the process of British Patent Application

5 No. 7921290 and also removal of the hop oils in the second pressure reduction vessel are complete, the base extract is removed from the pressure reduction vessel.

10 Instead of a base extract obtained by CO₂ extraction, it is also possible to use extracts obtained in another manner, for example those produced in the isomerisation process with the aid of organic solvents.

In order to enlarge the surface area of the resin-like
15 base extract and also to promote the formation of hulupone salts, the base extract is mixed with adsorbents, as a result of which a pulverulent extract is formed. Suitable adsorbents for use in the present invention are all conventional adsorbents, such as,
20 for example, activated charcoal, activated aluminium oxide, Fuller's earth, sodium bentonite, calcium bentonite, silica gel, kieselguhr and the like and also the known alkali and alkaline earth metal salts and their oxides or hydroxides, which are fixed by
25 lupulones and/or hulupones by adhesion, with salt formation. These include, in particular, Na₂CO₃, MgCO₃, CaCl₂, calcium oxide, magnesium oxide, sodium hydroxide and also potassium hydroxide.

The base extract which has been mixed with one
30 or more of the aforementioned carriers is also treated with one or more oxidising agents. Oxidising agents suitable for use in the present invention are, besides pure oxygen and the oxygen of the atmosphere, all known oxidants which can be used without
35 leaving a detrimental residue in an end product which is intended for food purposes.

It should be understood that the term liquid CO₂ as used herein means not only carbon dioxide which is subcritical with respect to pressure and temperature,
40 but also carbon dioxide which is sub-critical with respect to its temperature only (that is to say at or below 31.3°C), and which can also definitely have higher pressures than the pressure corresponding to the critical pressure of about 73 bars (for example, a
45 pressure of 200 bars and a temperature of 28°C).

The term supercritical CO₂ as used herein means carbon dioxide which has a temperature higher than 31.3°C and at the same time a pressure higher than 73 bars.

50 It was surprising to find that the formation of bitter-tasting hulupones, associated with a purification of these hulupones from the aforementioned undesirable and undefinable soft resins, esters and waxes takes place only as a result of the action of
55 liquid or supercritical CO₂.

This conversion into bitter-tasting hulupones and the purification of the same by means of CO₂ under the conditions of the present invention would not have been expected, since hitherto it was only
60 known that crude hulupones are formed from lupulones in the presence of an alkali and/or oxidising agents. This is especially unexpected since CO₂ is neither an oxidising agent nor a substance with an alkaline reaction.

65 The pressure treatment with CO₂ according to the

present invention therefore constitutes a conversion of the lupulones into bitter-tasting hulupones and includes the purification of the hulupones thus obtained.

70 The base extract which has been pretreated by the process of the present invention is conveyed into the extraction vessel of a CO₂ high-pressure apparatus and is there treated with CO₂, e.g. liquid or supercritical CO₂. Excess CO₂, which is charged with the
75 undesirable soft resins, esters and waxes, is continuously discharged into a pressure reduction vessel through a pressure controlled pressure reduction valve.

The action of the circulating CO₂ ensures that, at
80 the end of the extraction, only the bitter-tasting hulupones and/or salts thereof, together with the adsorbents used, are still present in the extraction vessel in the form of a pulverulent substance. The pulverulent hulupones which are removed from the
85 pressure vessel are then subjected to a process of fine comminution and can subsequently be added directly to the finished beer either on their own or else mixed with iso-alpha-acids which have been obtained in accordance with the process of British
90 Patent Application No. 7921290. The addition of quantities of hulupones, as compared with the addition of equivalent quantities of isohumulones to beer which was ready for drawing off, showed no significant differences in the purity of the odour of
95 the beer, in the purity of its taste, in the intensity and quality of its bitter taste nor in the body of the beer. In terms of the intensity of the bitter taste, the addition of hulupones obtained in accordance with the present invention leads to a saving in the
100 quantity of isohumulones added as a bitter constituent which corresponds to the amount of hulupones added.

The hulupones obtained in accordance with the present invention, in combination with the isohumulones obtained in accordance with the process of
105 British Patent Application No. 7921290, provides a beer-soluble product, as a bitter constituent, which has all the taste properties of natural hops.

110 Example

500 g of base extract which is freed from oil (β-acid content 49% on an anhydrous basis) is mixed with 500 g of sodium bentonite, and the mixture obtained is then treated for 2 hours in a pressure vessel under a
115 pressure of 250 bars by sucking in and blowing out air through two interposed pressure reduction valves.

Subsequently to the above oxidative treatment, the pulverulent base extract present in the pressure vessel is treated for 3 hours by passing there in supercritical
120 CO₂ at 70°C and under a CO₂ pressure of 350 bars.

During this treatment time, the undefinable resins (soft resins and hard resins), waxes and esters which are charged with CO₂ are separated off in portions at a time interval of about every 7 seconds through a pressure
125 reduction valve into a pressure reduction vessel at a pressure of 50 bars and a temperature of 21°C.

The yellow, resin-like mass obtained in the pressure reduction vessel is nearly free from β-acids, while the pulverulent product remaining in the pressure vessel is also free from β-acids.
130

When dissolved in water, the filtrate from the pulverulent product exhibits an intense and agreeably bitter taste. The substances having the taste have been identified as hulupones by means of thin layer chromatography.

CLAIMS

- 10 1. A process for obtaining hop extracts which comprises adding adsorbents to hop products which contain alpha acids and ground, crushed or ruptured lupulin seeds, or such hop products which are in the form of extracts, treating the mixture obtained with
15 CO₂ in a closed pressure vessel at a supercritical temperature and under a pressure of from 50 to 600 bars, reducing the pressure of the CO₂ leaving the pressure vessel whereby a base extract comprising hop oils and lupulones is precipitated, mixing the
20 lupulones with adsorbents, converting the lupulones to bitter-tasting hulupones by oxidation and treatment with CO₂ under pressure, and removing undesirable accompanying substances to purify the thus obtained hulupones.
- 25 2. A process as claimed in claim 1 wherein hop products in the form of extracts are used.
3. A process as claimed in claim 2 wherein the extracts are obtained by a process which comprises extracting hops or a hop product with CO₂ at a
30 temperature up to its critical temperature and at a pressure above its critical pressure and subsequently evaporating the CO₂ from the extract obtained.
4. A process as claimed in any of claims 1 to 3 wherein the hop oils contained in the base extract
35 are separated from the lupulones by reducing the pressure of the CO₂ in stages.
5. A process as claimed in claim 4 wherein in a first stage the CO₂ pressure is reduced to from 15 to 50% of the pressure prevailing in the pressure
40 vessel, and in a second stage the CO₂ pressure is reduced to from 50 to 80% of the pressure in said first stage.
6. A process as claimed in any of claims 1 to 5 wherein atmosphere oxygen is used as the oxidising
45 agent in the oxidation stage.
7. A process as claimed in any of claims 1 to 5 wherein a suitable oxidant (as herein defined) is used as the oxidising agent in the oxidation stage.
8. A process as claimed in any of claims 1 to 7
50 wherein adsorbents are added to the base extract for purifying the bitter-tasting hulupones.
9. A process as claimed in any of claims 1 to 8 wherein a pressure treatment with CO₂ in which the pressure of the CO₂ is reduced continuously is
55 carried out for converting the lupulones into bitter-tasting hulupones and for the purification thereof.
10. A process as claimed in any of claims 1 to 9 wherein the conversion of the lupulones into bitter-tasting hulupones and the purification thereof is
60 carried out in the pressure vessel using liquid CO₂, the pressure of the CO₂ being reduced continuously.
11. A process as claimed in any of claims 1 to 9 wherein the conversion of the lupulones to bitter-tasting hulupones and the purification thereof is
65 carried out in the pressure vessel using CO₂ above

its critical point, the pressure of the CO₂ being reduced continuously.

12. A process as claimed in any of claims 1 to 11 which further comprises the step of adding the
70 hulupones obtained, optionally together with isomerised alpha-acids to an alcohol-containing or an alcohol-free beverage which is to be made bitter.

13. A process for obtaining hulupones substantially as herein described with reference to the

- 75 Example.

14. Hulupones whenever obtained by a process as claimed in any of claims 1 to 12.

15. Substances whenever obtained by a process as claimed in any of claims 1 to 13.

- 80 16. Beer containing hulupones as claimed in claim 14.

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